

# THE TEMPERATURE DEPENDENCE OF INTER-DIFFUSION COEFFICIENT FOR SOME PAIRS OF RARE GASES

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**ABSTRACT.** The inter-diffusion coefficients for the three gas pairs He-Ne, He-Kr and Ne-Xe have been determined at 0°, 15°, 30° and 45°C. The diffusion takes place between two bulbs separated by a precision capillary tube. Samples of the gas are withdrawn from one bulb at different intervals of time and analysed by a differential conductivity analyser. These experimentally determined diffusion coefficients have been utilised for calculating the unlike potential parameters  $\epsilon_{12}$  and  $\sigma_{12}$  on the Lennard-Jones (12 : 6) model and compared with the values determined from the usual combination rules. The agreement is found to be satisfactory. The experimentally determined values of  $\epsilon_{12}$  and  $\sigma_{12}$  reproduce the experimental data on inter-diffusion quite satisfactorily. By utilising Kelvin's method, self-diffusion coefficients have been calculated from inter-diffusion coefficient data and the results have been compared with the experimental data when they are available.

## INTRODUCTION

The influence of intermolecular forces on gaseous transport properties has long been recognised and a great deal of information concerning like molecular interactions has been obtained from the determinations of the coefficient of viscosity of pure gases as a function of temperature, but corresponding information on forces between unlike molecules obtained directly from measurements on gaseous mixtures is very meagre. The most suitable transport property for studying unlike molecular interactions is inter-diffusion coefficient, for it depends in the first approximation only on the force fields of the unlike diffusing molecules and is independent of the like interactions. Thus  $\epsilon_{12}$  and  $\sigma_{12}$  can best be determined from the experimental data on inter-diffusion but unfortunately little work has been done so far in this field. Further, the available data are usually confined to one or two temperatures only and hence no reliable information can be obtained from them. Recently, Srivastava and Srivastava (1959) and Srivastava (1959) have determined the coefficients of inter-diffusion for the gas pairs Ne-A, Ne-Kr, A-Kr and A-He, A-Xe, He-Xe. In the present investigation the inter-diffusion coefficients for the gas pairs He-Ne, He-Kr, Ne-Xe at 0°, 15°, 30° and 45°C, have been measured.

## APPARATUS

The diffusion apparatus consists of two bulbs connected by a specially designed brass capillary tube and stop-cock. The bulbs are immersed in a thermostat bath which is maintained at temperatures  $0^{\circ}$ ,  $15^{\circ}$ ,  $30^{\circ}$ , and  $45^{\circ}\text{C}$  to  $\pm 0.01^{\circ}\text{C}$ . A detailed account of the diffusion apparatus used has been given by Srivastava and Srivastava (1959).

For analysing the gas mixture a differential conductivity analyser essentially similar to the one employed by Grew (1954) was designed and constructed as shown in figure 1. A precision conductivity cell of stainless steel of the type described by Srivastava and Saxena (1957) is constructed with a platinum wire  $0.075\text{ mm.}$  in diameter mounted axially and insulated at one end with Perspex cap. A compression unit capable of compressing the gas upto twenty times, together with a sensitive manometer, is permanently sealed to the above cell by cold setting Araldite adhesive. Two such units form the two arms of a Wheatstone bridge, one of the cells containing a suitable standard gas (heavier) while the other a sample of the gas to be analysed. Two fixed manganin resistors of S.W.G.

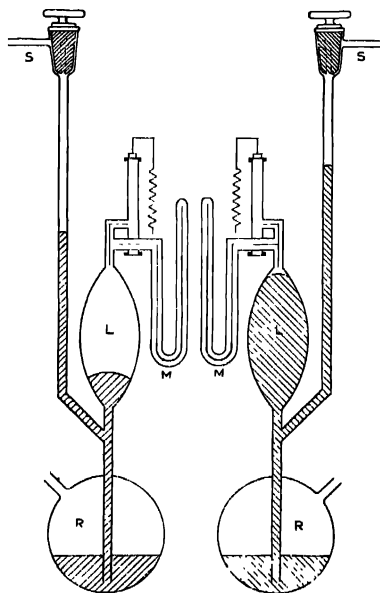


Fig. 1

20 of about 3 ohms resistance forming the other two arms of the bridge are mounted close to the conductivity cells.

It was observed that at a pressure of 6 cm. of Hg or more, the wire resistance is insensitive to the change of pressure and therefore all the samples were compressed to 6 cm. of Hg, and this was kept the same for calibration and also for analysis. For greater accuracy and stability the conductivity analyser as well as the two resistances in the other arms of the bridge circuit are immersed in an oil thermostat controlled at  $35^{\circ}\text{C} \pm 0.05^{\circ}\text{C}$  by efficient stirring in conjunction with a spiral type mercury-ether thermal regulator and electronic relay. The analyser takes only 0.3 cc. of gas at N.T.P. for analysis and therefore the pressure of the gas in the two diffusion bulbs is not disturbed.

The two conductivity cells, each of about 1.3 ohms resistance and the two fixed resistors are placed close to each other in the same thermostat to obtain steady and reproducible conditions. A variable resistance of W. G. Pye (accurate to 0.02%) adjustable to 0.01 ohm resistance is placed in parallel to one of the fixed resistors and serves to balance the bridge. The bridge is fed by a constant current of about 0.3 ampere from a high capacity battery with a standard resistance and fine rheostat included in the circuit, the rheostat being adjusted to keep the e.m.f. across the standard resistance constant as read on a vernier potentiometer reading upto  $1\mu\text{V}$  with an accuracy of  $\pm 0.004\%$ . The value of the parallel

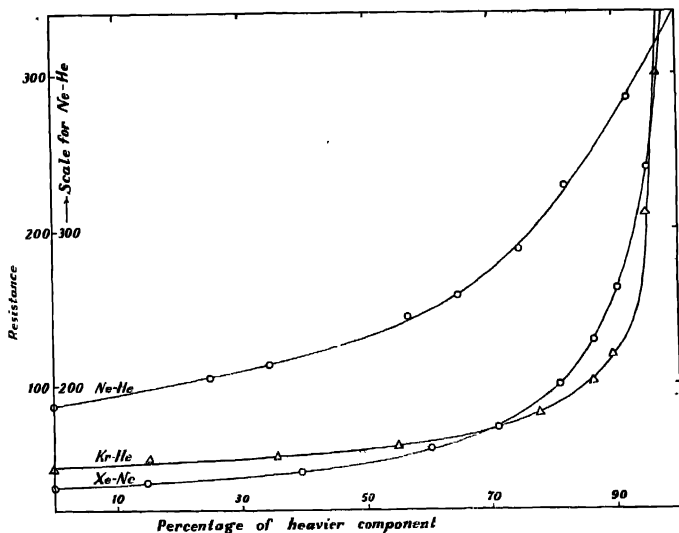


Fig. 2

resistance is adjusted to be about 500 ohms when both the cells of the analyser are filled with the heavier gas at the same pressure. When a mixture of unknown composition is introduced in one of the cells, the bridge balance is disturbed and the parallel resistance is carefully adjusted to restore the balance as read on a voltage sensitive galvanometer (Cat. No. 7940) of W. G. Pye.

For each gas mixture values of the parallel resistance required to balance the bridge for different compositions of the gas mixture are observed and a calibration curve plotted (figure 2) giving the composition of the mixture for any value of the parallel resistance. Considering the accuracy of the electrical circuit and the error involved in making a mixture of known composition it is believed that the error in the composition of the mixture as determined from the calibration curve is about  $\pm 0.05\%$

#### EXPERIMENTAL PROCEDURE

The dimensions of the diffusion capillary are first determined and then it is fitted vacuum tight to the two diffusion bulbs. The two bulbs are then evacuated to about  $10^{-3}$  mm. of Hg. by a two stage rotary pump. The heavier gas is first allowed to fill both the diffusion bulbs at the desired pressure which is read on a manometer with help of a cathetometer. One of the gas filled bulbs is cut off from the vacuum circuit by operating the stop-cock connecting the two bulbs and then the other bulb is evacuated. The other gas is then filled in the evacuated bulb and the pressure adjusted to be the same in both the bulbs. After allowing sufficient time to the bulbs to attain the temperature of the bath, diffusion is started by opening the stop-cock connecting the two bulbs. Samples of the gas are drawn through the capillary leak at suitable intervals. The analyser is highly evacuated by an oil diffusion pump and the order of vacuum attained is read on a Pirani gauge. Gas from one of the diffusion bulbs is allowed to leak into the analyser for one minute and then compressed to the desired pressure and the value of the resistance required to balance the bridge is determined. The middle of the interval of one minute is taken as the time at which the composition is determined.

#### THEORY AND FORMULAE

The theory of this method has been fully discussed by Ney and Armistead (1947) who showed that the relaxation time  $1/\alpha$  of the system defined by the relation

$$\frac{C_1^t - C_1^\infty}{C_1^0 - C_1^\infty} = \exp(-\alpha t) \quad \dots (1)$$

is given by

$$\alpha = \frac{D_p A}{l} \left( \frac{V_0}{V_1 V_2} \right) \quad \dots (2)$$

where  $C_1^0$ ,  $C_1^t$  and  $C_1^\infty$  are respectively the concentrations of the heavier gas initially, at time 't' seconds, and after complete mixing,  $V_1$  and  $V_2$  are the volumes of the two bulbs in cc. and  $V_0 = V_1 + V_2$ .  $D_p$  is the coefficient of diffusion in cm<sup>2</sup>/sec at the pressure of  $p$  cm. of mercury.  $A$  and  $l$  are respectively the effective cross-sectional area and effective length of the diffusion path.

A graph connecting  $\log_e(C_1^t - C_1^\infty)$  and  $t$  is plotted which gives a straight line the slope of which determines  $-\alpha$ . This is substituted in Eq. (2) to give  $D_p$  at the pressure  $p$  of the gas. In the actual experiment the diffusion path consists of several sectors of varying  $l/A$ , the volume of the diffusion path being negligible as compared to the volume of the diffusion bulbs. Eq. (2) is then written

$$\alpha = D_p \sum \frac{A_j}{l_j} \left( \frac{V_0}{V_1 V_2} \right) \quad \dots (3)$$

where  $A_j$  and  $l_j$  refer to the various sectors of the diffusion path.

#### EXPERIMENTAL RESULTS

The gases used in the present investigation were supplied by the British Oxygen Co., England; helium was quoted as spectroscopically pure while krypton and xenon contained some traces of impurities.

TABLE I

Observed concentration of the heavier components at different times for He-Ne, He-Kr, Ne-Xe at 0°C for all gas pairs  $C_1^\infty = 0.373$

Gas Pair	Time in mins	Resistance in ohms	$C_1^t$	$\log_{10}(C_1^t - C_1^\infty)$
He-Ne	0	..	1.0	.7913
	20	326.0	0.820	.6500
	34	281.5	0.721	.5422
	55	250.3	0.612	.3787
	90	231.8	0.499	.1000
He-Kr	0	..	1.0	.7973
	23	152.0	0.870	.6964
	50	113.4	0.745	.5700
	82	87.8	0.636	.4200
	118	76.0	0.559	.2701
Ne-Xe	0	..	1.0	.7973
	50	152.0	0.893	.7160
	80	113.4	0.839	.6680
	120	87.8	0.771	.6001
	160	76.0	0.721	.5420

After a careful flushing of the leak tubes, the gas from one of the diffusion bulbs was allowed to leak into the analysis cell of the differential conductivity analyser. This was done at four different intervals of time and the gas was analysed to give  $C_1^t$ . Tables I-IV show the observations for all gas pairs at 0°, 15°, 30° and 45°C.  $\log_{10} (C_1^t - C_1^\infty)$  versus  $t$  were plotted and found to be straight lines whose slope determined  $\alpha$ .  $C_1^\infty$  is calculated from the initial concentrations of the two bulbs and later on checked experimentally by determining the concentration after a time interval greater than several multiples of the relaxation time.

TABLE II

Observed concentration of the heavier components at different times for He-Ne, He-Kr, Ne-Xe at 15°C. For all gas pairs  $C_1^\infty = 0.373$

Gas Pair	Time in mins	Resistance in ohms	$C_1^t$	$\log_{10} (C_1^t - C_1^\infty)$
He-Ne	0	..	1.0	1.7973
	20	311.0	0.790	.6205
	30	280.3	0.720	.5400
	45	252.4	0.625	.4005
	70	235.3	0.525	.1810
He-Kr	0	..	1.0	.7973
	18	102.0	0.863	.6900
	50	70.0	0.697	.5100
	70	64.3	0.621	.3950
	106	60.0	0.527	.1883
Ne-Xe	0	..	1.0	.7973
	40	157.0	0.898	.7204
	80	99.3	0.808	.6381
	120	78.8	0.734	.5580
	160	68.0	0.675	.4804

The quantity  $D/\alpha$  which is a constant independent of the mixture used is determined previously from the measured geometric constants of the apparatus with the help of Eq. (3). Thus knowing  $\alpha$ , the value of  $D_p$  for the gas pair is determined at the pressure of the gas. It is then converted into the diffusion coefficient at atmospheric pressure by the relation

$$D_{atm} = \frac{D_p \cdot p}{760} \quad (4)$$

where  $p$  is the pressure of the gas in *mm.* of Hg. The experimental values of  $D_{12}$  thus obtained are collected in table V for all the gas pairs, the last column

TABLE III

Observed concentration of the heavier components at different times for He-Ne, He-Kr, Ne-Xe at 30°C. For all gas pairs  $C_1^\infty = 0.373$

Gas Pair	Time in mins	Resistance in ohms	$C_1^t$	$\frac{\log^{10}}{(C_1^t - C_1^\infty)}$
He-Ne	0	.	1.0	1.7973
	15	330.5	0.832	.6620
	24	284.0	0.730	.5531
	41	250.6	0.616	.3857
	61	235.2	0.528	.1900
He-Kr	0	..	1.0	.7973
	20	95.5	0.841	.6701
	46	69.8	0.689	.5003
	71	63.0	0.682	.3430
	113	58.8	0.491	.0701
Ne-Xe	0	..	1.0	.7973
	38	95.5	0.886	.7100
	90	69.8	0.771	.6002
	135	63.0	0.682	.4900
	168	58.8	0.636	.4203

giving the value of  $D_{12}$  at atmospheric pressure. The various sources of error in this method have been fully discussed by Ney and Armistead (1941) and Srivastava and Srivastava (1959). The values of  $D_{12}$  obtained in the present paper are believed to be accurate to within 1%.

#### DETERMINATION OF FORCE CONSTANTS

Srivastava and Srivastava (1959), Bunde (1958) and Strohlow (1953) have discussed the various methods employed for determining force constants from the diffusion data. These methods are : (1) The ratio method, (2) the translational method of Keesom (1912) and Lennard-Jones (1924), (3) the intersection method of Buckingham (1938), (4) Combination method utilising binary viscosity or conductivity in addition. Srivastava and Srivastava (1959) have discussed the limitations and difficulties of methods (1) and (2). These fail to give any suitable force

TABLE IV

Observed concentration of the heavier components at different times for He-Ne, He-Kr, Ne-Xe at 45°C. For all gas pairs  $C_1^\infty = 0.373$

Gas Pair	Time in mins	Resistance in ohms	$C_1^t$	$\log^{10} (C_1^t - C_1^\infty)$
He-Ne	0	..	1.0	1.7973
	20	274.2	0.704	.5203
	40	239.1	0.552	.2519
	60	228.0	0.470	2.9851
He-Kr	0		1.0	1.7973
	21	94.8	0.84	.6702
	42	72.2	0.724	.5449
	58	66.6	0.665	.4408
	85	62.0	0.568	.2903
Ne-Xe	0		1.0	.7973
	36	135.5	0.874	.7000
	88	84.0	0.758	.5850
	126	69.1	0.682	.4902
	176	59.7	0.607	.3703

TABLE V

Observed values of the Diffusion Coefficient.

Gas Pair	Temp °K	Pressure (mm. of Hg.)	$D_p$ (cm <sup>2</sup> /sec)	$D_{atm}$ (cm <sup>2</sup> /sec)
He-Ne	273	89.26	7.715	0.906
	288	84.84	8.833	0.986
	303	82.02	9.868	1.065
	318	71.16	12.37	1.158
He-Kr	273	92.64	4.561	0.556
	288	79.98	5.749	0.605
	303	77.56	6.458	0.650
	318	89.32	6.127	0.720
Ne-Xe	273	85.08	1.662	0.186
	288	78.32	1.960	0.202
	303	78.54	2.139	0.221
	318	74.58	2.481	0.244



constants in the present case. Methods (3) and (4) have been carried out quite successfully and are given below:

Method 3. The method can yield the force constants even if the experimental data are limited to only two temperatures, not far apart, provided the data are highly accurate. The diffusion equation is solved for the collision diameter  $\sigma_{12}$ , as

$$\sigma_{12} = \frac{0.002628 [T^3 (M_1 + M_2) / 2 M_1 M_2]^{\frac{1}{2}}}{D_{12} p \Omega_{12}(1,1)^* (T_{12}^*)} \quad (5)$$

where  $D_{12}$  is the mutual diffusion coefficient in  $\text{cm}^2/\text{sec}$ ,  $p$  is the pressure in atmospheres,  $\sigma_{12}$  in Angstroms, and  $\Omega_{12}(1,1)^*$  is a reduced collision integral tabulated by Hirschfelder, Curtiss and Bird (1954). The higher approximation term coming through the factor  $f_{D_{12}}^{(m)}$  is always close to unity and has therefore been neglected. For arbitrarily selected values of  $\epsilon_{12}$  a series of mutually consistent values of  $\epsilon_{12}$  and  $\sigma_{12}$  are determined from Eqn. (5) and a graph plotted with  $\epsilon_{12}$  as abscissa and  $\sigma_{12}$  as ordinate. Such a graph is drawn for each experimental value of  $D_{12}$  and the best value of the intersection point fixes up  $\epsilon_{12}$  and  $\sigma_{12}$ . In practice it is difficult to obtain one unique point of intersection for all the curves due inherently to the fact that the  $D_{12}$  data are not very accurate. Different intersection points yield a range of values of  $\epsilon_{12}$  and  $\sigma_{12}$  and these are averaged to give a mean value. The values are collected in Table VI column 3.

Method 4. The diffusion equation and the expression for the binary viscosity,  $\eta_{m1x}$ , are solved together to eliminate  $\sigma_{12}$ . The solution involves the only temperature dependent factor  $A_{12}^*$  which can be put in the convenient form

$$A_{12}^* = \frac{1 - \eta_{m1x} \left[ \frac{x_1^2}{\eta_1} + \frac{x_2^2}{\eta_2} \right] + \frac{3}{10} \frac{x_1 x_2}{\eta_1 \eta_2} \frac{(M_1 + M_2)^2}{M_1 M_2} \eta_0 [\eta_1 + \eta_2 - \eta_{m1x}]}{2 x_1 x_2 \left( \frac{\eta_{m1x}}{\eta_0} \right) + \frac{3}{5} \frac{x_1^2}{\eta_1} \left( \frac{M_1}{M_2} \right) [\eta_{m1x} - \eta_1] + \frac{3}{5} \frac{x_2^2}{\eta_2} \left( \frac{M_2}{M_1} \right) [\eta_{m1x} - \eta_2] + \frac{6}{5} x_1 x_2 \dots} \quad (6)$$

where  $\eta_1$ ,  $\eta_2$  are the viscosities of the pure components and  $M_1$ ,  $M_2$  and  $x_1$ ,  $x_2$  are respectively their molecular weights and molar fractions  $\eta_0$  is given by the expression

$$\eta_0 = \frac{266.93}{0.002628} \left[ \frac{2 M_1 M_2}{(M_1 + M_2)} \right] \times \frac{D_{12}}{T} \times 10^{-7} \quad \dots \quad (7)$$

From a knowledge of  $\eta_{m1x}$ ,  $\eta_1$ ,  $\eta_2$ ,  $D_{12}$ , the quantity  $A_{12}^*$  may be obtained with the help of Eqn. (6). The corresponding value of  $T_{12}^*$  is read from the table given by Hirschfelder, Curtiss and Bird (1954), which ultimately determines  $\epsilon_{12}/k$  from the relation  $T_{12}^* = kT/\epsilon_{12}$ . Eqn. (5) is then used to fix up the value of  $\sigma_{12}$ .

This is repeated for each temperature and the values of  $\sigma_{12}$  thus obtained are averaged. The values of  $\epsilon_{12}/k$  and  $\sigma_{12}$  are listed in column 4 of table VI. These may be compared with the values obtained previously from thermal diffusion data by Saxena (1955) and also those obtained with the usual combination rules viz.  $\epsilon_{12} = (\epsilon_1 \times \epsilon_2)^{1/2}$  and  $\sigma_{12} = \frac{1}{2}(\sigma_1 + \sigma_2)$ . These are respectively given in columns 5 and 6 of table VI.

The values of the force constants given in column 4 are believed to be more accurate than those recorded in column 3. They have, therefore, been used to calculate the mutual diffusion coefficient of the different gas pairs on the Lennard-Jones (12 : 6) model and the calculated values compared with the experimentally observed values in table VII. The agreement between calculated and experimental values of  $D_{12}$  is found to be very close which shows that the force constants derived by us are quite reliable and can be used to calculate other transport properties.

#### SELF-DIFFUSION

It is possible to calculate self-diffusion coefficient of gases on the rigid sphere model by combining inter-diffusion coefficient data for different triads of gases which give the self-diffusion coefficient for each of the gases forming the triad.

TABLE VI

Potential parameters on the Lennard-Jones (12 : 6) model from experimental data

Gas Pair	Force Parameters	Intersection method	From combination of $D_{12}$ and $\eta_{mix}$	From thermal diffusion	From combination rules
He-Ne	$\epsilon_{12}/k$	18.6	20.19	....	19.11
	$\sigma_{12}$	2.681	2.662	....	2.683
He-Kr	$\epsilon_{12}/k$	46.0	....	....	44.07
	$\sigma_{12}$	3.084	....	....	3.093
Ne-Xe	$\epsilon_{12}/k$	91.5	....	71.99	90.42
	$\sigma_{12}$	3.377	.. .	3.460	3.422

The method of calculation of self-diffusion coefficient which is due to Kelvin is as follows :—

For rigid elastic spheres the first approximation to the coefficient of inter-diffusion of two gases 1 and 2 is

$$[D_{12}]_1 = \frac{3}{8(n_1 + n_2)\sigma_{12}^2} \left[ \frac{kT(m_1 + m_2)}{2\pi m_1 m_2} \right]^{1/2} \quad \dots (8)$$

TABLE VII

Comparison of observed values of the mutual diffusion coefficient with those calculated from the force parameters derived from the experimental data. Values of  $D_{12}$  are expressed in  $\text{cm}^2/\text{sec}$ .

Temp °K Gas Pair	273	288	303	318
<hr/>				
He-Ne				
Expt.	0.996	0.986	1.065	1.158
Calc.	0.901	0.984	1.070	1.160
<hr/>				
He-Kr				
Expt.	0.556	0.605	0.659	0.720
Calc.	0.554	0.604	0.660	0.718
<hr/>				
Ne-Xe				
Expt.	0.186	0.202	0.221	0.244
Calc.†	0.185	0.203	0.222	0.242

\*All data at one atmosphere.

† Calculated from the force parameters given in Column 4 of table VI.

where  $m_1, m_2$  are the masses of the molecules 1 and 2,  $n_1$  and  $n_2$  their number densities and  $\sigma_{12}$  the collision diameter for the pair of gases.

$\sigma_{12}$  may be calculated from Eqn.(8) by utilising the experimental value of  $D_{12}$ . From the triad of gases 1-2-3 we can determine  $\sigma_{12}, \sigma_{23}, \sigma_{13}$  and since  $\sigma_{12} = \frac{1}{2}(\sigma_1 + \sigma_2)$  with similar expressions for  $\sigma_{23}$  and  $\sigma_{13}$  we can find  $\sigma_1, \sigma_2, \sigma_3$ . Then the self-diffusion coefficient for the same temperature may be determined from the relation

$$[D_{11}]_1 = \frac{3}{8n\sigma_{11}^2} \left[ \frac{kT}{\pi m} \right]^{\frac{1}{2}} \quad \dots \quad (9)$$

Recently Srivastava and Srivastava (1959) and Srivastava (1959) have given the data on inter-diffusion for the gas pairs Ne-A, A-Kr, Ne-Kr, A-He, A-Xe, He-Xe at 0°, 15° 30° and 45°C. By utilising Kelvin's method, they have also calculated self-diffusion coefficients for He, Ne, A, Kr, Xe on the rigid sphere model. The values thus obtained have been compared with the experimental values. We have combined the inter-diffusion coefficients at N.T.P. for all the gas pairs reported in this paper and those reported by Srivastava and Srivastava (1959) and Srivastava (1959) to yield the values of the self-diffusion coefficient. The results of calculation are shown in Table VIII. Only for Ne, A, experimental data are available at N.T.P. The calculated values of  $D_{11}$  for Ne, A, are found to be in fair agreement with the experimental values.

TABLE VIII  
Coefficient of self-diffusion (at N.T.P.)

Combination of gases used	Coefficients of self-diffusion cm <sup>2</sup> /sec.				
	He	Ne	A	Kr	Xe
Ne-A-Kr	..	0.520	0.152	0.087	..
A-He-Xe	2.548	..	0.136	...	0.055
He-Ne-Kr	1.052	0.589	....	0.084	...
He-Ne-Xe	1.086	0.482	..	...	0.059
A-He-Kr	1.892	..	0.150	0.090	...
A-Ne-Xe	..	0.565	0.142	..	0.047
Mean	1.945	0.540	0.148	0.087	0.053
Expt	..	0.462	0.156	..	..

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